[CONTRIBUTION NO. 887 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

# The Synthesis of Certain Ketones and α-Substituted β-Diketones Containing Perfluoroalkyl Groups

BY LLOYD B. BARKLEY[1] AND ROBERT LEVINE

RECEIVED DECEMBER 13, 1952

A study has been made of the synthesis of α-methylbenzoyltrifluoroacetone, MBTA, by the acylation of propiophenone with methyl trifluoroacetate in the presence of sodium methoxide. The reaction is complicated by the formation of cleavage products and the extent to which cleavage occurs depends on both the amount of base used and reaction time. Several other α-methyl and α-ethyl substituted β-diketones containing the $CF_3$ group have been synthesized. Four ketones of the type $C_xF_{2x+1}COC_nH_{2n+1}$ have been prepared and it has been found that $CF_3COC_3H_7$-*n* and $CF_3COCH_2C_6H_5$ undergo O- rather than C-acylation when their sodium derivatives are treated with benzoyl chloride.

In connection with the current interest[2] in the use of β-diketones containing perfluoroalkyl groups as chelating agents, we recently reported[3] the synthesis of a number of such compounds of the type $RCOCH_2COC_nF_{2n+1}$, where R is an alkyl, aryl or heterocyclic radical and *n* is 1 or 3. In the present paper we report the direct synthesis of α-substituted derivatives of a few of the previously reported fluorinated β-diketones and the preparation of several fluorinated ketones.

The one reported direct synthesis of an α-substituted β-diketone containing a perfluoroalkyl group is the preparation of α-methylpropionyltrifluoroacetone in 45% yield by the interaction of diethyl ketone with ethyl trifluoroacetate in the presence of sodium methoxide.[4]

We first studied the synthesis of α-methylbenzoyltrifluoroacetone, MBTA.

$$C_6H_5COCH_2CH_3 + CF_3CO_2CH_3 \xrightarrow{NaOCH_3} CH_3OH + C_6H_5COCH(CH_3)COCF_3$$

Using equivalents of reactants and a 20-hour reaction time and working up the reaction by the copper salt method[5] gave only 5% of MBTA; but a 30–35% yield of product could be obtained in the following way. At the end of the reaction, the mixture was poured onto ice and the basic and neutral phases separated. Acidification of the ice-cold basic phase gave MBTA and trifluoromethyl ethyl ketone (isolated as its 2,4-dinitrophenylhydrazone) and in the neutral phase methyl benzoate and propiophenone (determined by infrared analysis) were shown to be present. A possible course for the reaction is shown below. Equations 1, 2 and 3a

$$C_6H_5COCH_2CH_3 + NaOCH_3 \rightleftarrows \underset{\text{I}}{(C_6H_5COCHCH_3)^-Na^+} + CH_3OH \quad (1)$$

$$\text{I} + CF_3CO_2CH_3 \rightleftarrows \underset{\text{II}}{C_6H_5COCH(CH_3)COCF_3} + NaOCH_3 \quad (2)$$

$$\text{II} + NaOCH_3 \longrightarrow \left[\begin{array}{l} \overset{3a}{\rightleftarrows} (C_6H_5COC(CH_3)COCF_3)^-Na^+ + CH_3OH \\ \overset{3b}{\rightleftarrows} (C_6H_5COCHCH_3)^-Na^+ + CF_3CO_2CH_3 \\ \overset{3c}{\longrightarrow} (CF_3COCHCH_3)^-Na^+ + C_6H_5CO_2CH_3 \end{array}\right. \quad (3)$$

are those usually postulated for the base effected Claisen acylation of ketones[6] and there is much evidence that the cleavage of β-diketones (steps 3b and 3c) occurs through their keto rather than enol forms.[7–12]

It is impossible to determine the extent to which step 3b occurs during the synthesis of MBTA since it gives starting materials and is obviously reversible. The fact that we were able to show the presence of methyl benzoate and trifluoromethyl ethyl ketone in approximately equivalent yields in two experiments provides evidence for the occurrence of step 3c.

*The unique characteristics of step 3c are: (1) its apparent irreversibility and (2) the products of this cleavage appear not to react with any of the other compounds which are present in the reaction mixture.* These unusual facts distinguish the acylation of propiophenone with methyl trifluoroacetate, wherein only one β-diketone is formed, from the acylation of propiophenone with ethyl acetate,[13] wherein three β-diketones are formed due to the partial cleavage of the initial acylation product, α-methylbenzoylacetone, followed by recombination of the fragments produced.

---

[1] This paper is based on a portion of the thesis presented by Lloyd B. Barkley to the Graduate Faculty of the University of Pittsburgh in partial fulfillment of the requirements of the Ph.D. degree; present address: Monsanto Chemical Company, St. Louis, Missouri.

[2] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

[3] L. B. Barkley and R. Levine, THIS JOURNAL, **73**, 4625 (1951).

[4] J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

[5] G. R. Zellars and R. Levine, *J. Org. Chem.*, **13**, 160 (1948).

[6] See, for example, J. T. Adams and C. R. Hauser, THIS JOURNAL, **66**, 1220 (1944).

[7] W. Bradley and R. Robinson, *J. Chem. Soc.*, **129**, 2356 (1926).

[8] L. J. Beckham and H. Adkins, THIS JOURNAL, **56**, 1119 (1934).

[9] C. L. Bickel, *ibid.*, **67**, 2204 (1945).

[10] C. R. Hauser, F. W. Swamer and B. I. Ringler, *ibid.*, **70**, 4023 (1948).

[11] R. G. Pearson and E. A. Mayerle, *ibid.*, **73**, 926 (1951).

[12] Data are also available to support the hypothesis that in the alkaline hydrolysis or alcoholysis of an unsymmetrical β-diketone, the diketone is attacked predominantly by the base at that carbonyl carbon atom which will give the stronger acid or ester of the stronger acid (see references 7, 9 and 10). Since trifluoroacetic acid ($K$a = $5.0 \times 10^{-1}$) (F. Swarts, *Bull. Acad. Roy. Belg.*, 681 (1896); 624 (1903); 353 (1922)) is a considerably stronger acid than benzoic acid ($K$a = $6.6 \times 10^{-5}$) (N. A. Lange, "Handbook of Chemistry," 2nd Edition, p. 1156) one would expect that cleavage 3b would occur more rapidly and extensively than 3c. In the present study it was found that the cleavage of MBTA by aqueous sodium hydroxide gave an essentially quantitative yield of propiophenone (equation 3b) and no benzoic acid; while its cleavage with sodium methoxide gave a mixture of MBTA, propiophenone (step 3b) and methyl benzoate (step 3c), with the proportion of propiophenone far exceeding that of methyl benzoate.

[13] G. T. Morgan, H. D. K. Drew and C. R. Porter, *Ber.*, **58**, 333 (1925).

Since we were unable to isolate trifluoromethyl ethyl ketone in good yields and in a high state of purity, two experiments were performed with its homolog, trifluoromethyl *n*-propyl ketone, in order to obtain some evidence concerning the irreversibility of equation 3c. It was found that this ketone could not be acylated by either methyl benzoate or methyl trifluoroacetate in the presence of sodium methoxide[14]; and further, it was impossible to condense propiophenone with methyl benzoate in the presence of sodium methoxide.

In order to determine whether the yield of MBTA could be increased, variations in the quantities of base and in reaction time were considered. The pertinent data are summarized in Table I. It may be seen that by increasing the equivalents of base used from one to two, a yield of 61% of MBTA may be obtained. Furthermore, it may be noted that the yield of diketone was not raised by increasing the reaction time over 3.5 hours. Apparently, during the synthesis of MBTA there is a delicate balance between the total amount of β-diketone actually formed on the one hand, and the amount of β-diketone isolated and cleaved on the other. Using two equivalents of base, the β-diketone is synthesized and converted rapidly to its anion at the start of the reaction and not too much of it is cleaved in the early stages of the reaction. When the reaction time is increased over 3.5 hours, the yield of MBTA remains essentially constant and any more of the diketone which is produced is cleaved more rapidly than it is converted to its anion as indicated by the increase in the yield of methyl benzoate.

TABLE I

SYNTHESIS OF α-METHYLBENZOYLTRIFLUOROACETONE, MBTA[a]

| Sodium methoxide equivalents | Reaction time in hours | Products isolated, % Propiophenone | Methyl benzoate | MBTA |
|---|---|---|---|---|
| 0.5 | 20.0 | 70.6 | 24.4 | 1.5 |
| 1.0 | 1.1 | 82.7 | 0.0 | 8.4 |
| | 3.5 | 56.4 | 10.0 | 21.7 |
| | 20.0 | 30.3 | 28.4[b] | 32.1 |
| | 40.0 | 19.9 | 41.6 | 31.5 |
| 1.5 | 20.0 | 16.2 | 18.9 | 54.0 |
| 2.0 | 1.1 | 54.6 | 4.7 | 29.5 |
| | 3.5 | 20.6 | 9.1 | 61.0 |
| | 20.0 | 12.7 | 15.6[c] | 60.5 |
| | 40.0 | 10.2 | 17.5 | 60.0 |

[a] In all runs equivalents of ester and ketone were used. [b] Isolated 22.8% yield of $CF_3COC_2H_5$ as its 2,4-dinitrophenylhydrazone. [c] Isolated 12.5% yield of $CF_3COC_2H_5$ as its 2,4-dinitrophenylhydrazone.

In order to determine whether other ethyl ketones could be acylated satisfactorily with perfluoroalkyl esters, equivalents of three additional such ketones (diethyl ketone, 2-propionylthiophene and 2-propionylfuran) and ethyl trifluoroacetate were allowed to react for 20 hours with one and two equivalents of sodium methoxide. From Table II, in which the data on propiophenone have been included for the purpose of comparison, it may be seen that diethyl ketone gives the highest and 2-propionylfuran the lowest yield of the corresponding α-methyl substituted β-diketone when equivalents of reactants are used. These reasonable results may be explained in the following way. In β-diketones of the type $RCOCH(CH_3)COCF_3$, which differ from one another only in the nature of R, the extent of cleavage at the RCO carbonyl group should depend on the electrophilic character of the carbonyl carbon atom. The greater the extent of cleavage is at this group, the smaller will be the yield of the β-diketone which is isolated. In a series of β-diketones of the above structure in which R is the ethyl, phenyl, 2-thienyl or 2-furyl radical, based on electrical effects, it appears reasonable that the extent of cleavage at the RCO group should increase in the order in which these radicals are listed.[15] It may also be seen in Table II that the fair yields of β-diketones obtained with one equivalent of base are increased considerably when two equivalents of base are used since under the latter conditions cleavage of the β-diketones is greatly reduced.

In attempting to extend our methods to α-ethyl substituted β-diketones, di-*n*-propyl ketone and butyrophenone were acylated with ethyl trifluoroacetate in the presence of two equivalents of sodium methoxide. While a 34.2% yield of α-ethyl-*n*-butyryltrifluoroacetone was isolated from the former reaction, only 6% yield of α-ethylbenzoyltrifluoroacetone was obtained from the butyrophenone acylation.[16] However, in addition to the small amount of diketone, which was obtained in the latter experiment, a mixture of methyl and ethyl benzoates and trifluoromethyl *n*-propyl ketone (cleavage products) was obtained.

When it was found that the attempted acylation of butyrophenone with ethyl trifluoroacetate gave very little of the expected β-diketone and large amounts of cleavage products, the reaction mixture was worked up in such a way as to enable the isolation of the trifluoromethyl *n*-propyl ketone. The method was extended, as shown in the following scheme, to the synthesis of three other perfluoroalkyl alkyl ketones, *i.e.*, $CF_3COC_2H_5$ ($n = 1, x = 1$); $CF_3COC_5H_{11}$-*n* ($n = 4, x = 1$) and *n*-$C_3F_7COC_3H_7$-*n* ($n = 2, x = 3$). The pertinent data on these ketones are found in Table III.

$$C_6H_5COCH_2C_nH_{2n+1} + C_xF_{2x+1}CO_2CH_3 \xrightarrow{NaOCH_3} \underset{III}{C_6H_5COCH(C_nH_{2n+1})COC_xF_{2x+1}} + CH_3OH$$

$$III \xrightarrow{NaOCH_3} C_6H_5CO_2CH_3 + \underset{IV}{C_xF_{2x+1}COCH_2C_nH_{2n+1}}$$

Although it was not possible to acylate trifluoromethyl *n*-propyl ketone (IV, where $x = 1$, $n = 2$) with methyl benzoate in the presence of sodium

---

[14] It should be pointed out that the ketone might have been O-acylated by these esters but that the resulting enol esters were cleaved under the strongly basic reaction conditions.

[15] Some support for this statement is obtained from the ionization constants (at 25°) of the corresponding carboxylic acids; *viz.*, propionic, $Ka = 1.4 \times 10^{-5}$ (see ref. in footnote 12); benzoic, $Ka = 6.6 \times 10^{-5}$ (*ibid.*); 2-thiophenic, $Ka = 3.02\text{-}3.42 \times 10^{-5}$ (H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952); 2-furoic, $Ka = 7.1 \times 10^{-4}$ (Technical Bulletin, No. 101, The Quaker Oats Co., Chicago, Illinois, 1946).

[16] Even increasing the amount of base used to a reactant ratio of 1:1:5 of ketone, ester and base did not increase the amount of β-diketone isolated. It appears that the rate of synthesis of this diketone and conversion to its anion are always slower than its cleavage

TABLE II

β-DIKETONES OF THE TYPE $RCOCH(R')COCF_3$

| R | Ketone acetylated | $NaOCH_3$ equiv. | Yield, % | B.p., or m.p. °C. | Mm. | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Sulfur, % Calcd. | Sulfur, % Found | Copper salt, m.p., °C. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl | Diethyl | 1.0 | 50.5 | 148–151 | 735[b] | | | | | | | 163–165 |
| | | 2,0 | 63.7[a] | | | | | | | | | |
| | | 2.0 | 66.3 | | | | | | | | | |
| Phenyl | Propiophenone | 1.0 | 32.1 | 127–129 | 20 | 57.38 | 57.14 | 3.95 | 4.15 | | | 210–212[c] |
| | | 2.0 | 61.0[a] | | | | | | | | | |
| | | 2.0 | 60.5 | | | | | | | | | |
| 2-Thienyl | 2-Propionylthiophene | 1.0 | 30.8 | 116–119 | 9 | | | | | 13.58 | 13.36 | 202–204[d] |
| | | 2.0 | 62.0[a] | | | | | | | | | |
| | | 2.0 | 71.5 | | | | | | | | | |
| 2-Furyl | 2-Propionylfuran | 1.0 | 7.4 | 83–84.5 | 20 | 49.09 | 49.14 | 3.21 | 3.39 | | | 182–184[f] |
| | | 2.0 | 39.7[a] | | | | | | | | | |
| | | 2.0 | 40.6[e] | | | | | | | | | |
| 5-Methyl-2-thienyl | 5-Methyl-2-propionylthiophene | 2.0 | 62.3 | 146–148 | 20 | | | | | 12.82 | 12.97 | 231–234.5[g] |
| 2,5-Dimethyl-3-thienyl | 2,5-Dimethyl-3-propionyl thiophene | 2.0 | 74.6 | 143–145<br>M. 124–125.5 | 19 | | | | | 12.13 | 12.44 | 179–180.5[f] |
| 5-Methyl-2-furyl | 5-Methyl-2-propionylfuran | 2.0 | 75.0 | 121–124 | 20 | 51.28 | 51.34 | 3.88 | 4.11 | | | 169–171[g] |
| 2,5-Dimethyl-3-furyl | 2,5-Dimethyl-3-propionylfuran | 2.0 | 70.4 | 126–127<br>M. 83.5–85 | 20 | 53.22 | 52.98 | 4.88 | 4.56 | | | 172–174[h] |
| Phenyl | Butyrophenone[i] | 2.0 | 6.0 | 131–134 | 20 | 59.01 | 58.77 | 4.54 | 4.73 | | | [j] |
| *n*-Propyl | Di-*n*-propyl[i] | 2.0 | 34.2 | 113–114 | 98 | 51.43 | 51.35 | 6.23 | 5.98 | | | 146–147 |

[a] A 3.5-hour reaction time was used; in all other runs the reaction time was 20 hours. [b] See ref. 4. [c] Recrystallized from benzene. [d] Recrystallized from absolute ethanol. [e] Much tar also was formed. [f] Recrystallized from petroleum ether (60–70°). [g] Recrystallized from acetone. [h] Recrystallized from 95% ethanol. [i] R' is the ethyl radical; in all the ketones not marked, R' is the methyl radical. [j] This β-diketone appeared to give a copper salt, which could not be obtained in a crystalline state.

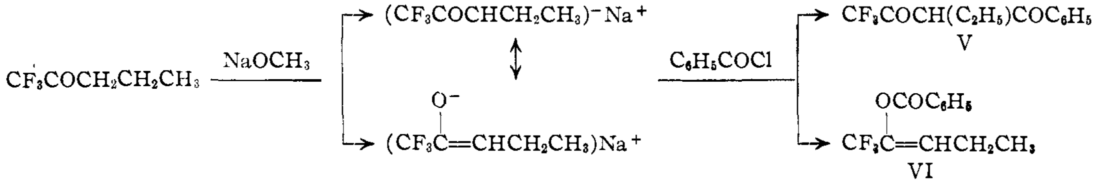
TABLE III

FLUORINATED KETONES

| Ketone acylated | Ester[a] | Fluorinated ketone | Yield, % | B.p., °C. | Mm. | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | 2,4-D,[e,f] m.p., °C. | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propiophenone | A[b] | Trifluoromethyl ethyl | 8.0 | 44–45 | 738 | ..[d] | ... | ... | ... | 91–92 | 18.30 | 18.40 |
| Butyrophenone | B[c] | Trifluoromethyl *n*-propyl | 43.0 | 65–67 | 735 | | | | | 73–73.5 | 17.50 | 17.58 |
| Caprophenone | B[c] | Trifluoromethyl *n*-amyl | 41.5 | 112–113.5 | 739 | | | | | 46–47 | 16.09 | 16.18 |
| Butyrophenone | C[c] | *n*-Heptafluoropropyl *n*-propyl | 51.5 | 99.5–101 | 741 | | | | | 37.5–38 | 13.32 | 13.53 |

[a] A, B and C are ethyl trifluoroacetate, methyl trifluoroacetate and ethyl *n*-heptafluorobutyrate, respectively. [b] Reactant ratio of equivalents of base, ester and ketone was 1:1:1. When the ratio was 2:1:1, the yield of product isolated was not increased. Under both of these sets of conditions, treatment of an aliquot portion of the reaction mixture with 2,4-dinitrophenylhydrazine showed the presence of much more $CF_3COC_2H_5$ than was isolated. [c] Reactant ratio of equivalents of base, ester and ketone was 2:1:1. [d] This compound behaved erratically on analysis. [e] 2,4-D means 2,4-dinitrophenylhydrazone. [f] Derivatives were recrystallized from 60–70° petroleum ether by cooling in a Dry Ice–acetone-bath.

methoxide to give the β-diketone, α-ethylbenzoyltrifluoroacetone, this ketone was acylated by benzoyl chloride in fair yield. In this latter reaction, either a β-diketone, V, (C-acylated product) and/or an enol ester, VI, (O-acylated product), as shown in the following scheme, could have been formed.



$$CF_3COCH_2CH_2CH_3 \xrightarrow{NaOCH_3} \left\{\begin{array}{l} (CF_3COCHCH_2CH_3)^-Na^+ \\ \updownarrow \\ (CF_3C(O^-)=CHCH_2CH_3)Na^+ \end{array}\right. \xrightarrow{C_6H_5COCl} \left\{\begin{array}{l} CF_3COCH(C_2H_5)COC_6H_5 \quad \text{V} \\ CF_3C(OCOC_6H_5)=CHCH_2CH_3 \quad \text{VI} \end{array}\right.$$

The reaction product was shown to be VI, 2-(1,1,1-trifluoro)-$\Delta^2$-pentenyl benzoate, since cleavage of a sample with aqueous alcoholic sodium hydroxide solution gave benzoic and *n*-butyric acids. An authentic sample of V, when treated similarly, gave a high yield of butyrophenone and no benzoic acid. Furthermore, V gives a red color with alcoholic iron(III) chloride solution and appeared to give a copper chelate when treated with aqueous copper(II) acetate; while both of these reactions are negative with VI. The infrared spectrum of VI showed no evidence of the presence of an hydroxyl group, while V shows hydroxyl absorption at 2.95 μ.

The sodium derivative of trifluoromethyl benzyl ketone was also acylated with benzoyl chloride in order to determine what effect, if any, the replacement of the ethyl group on the α-carbon atom of trifluoromethyl *n*-propyl ketone by a phenyl group would have on the nature of the product formed. Here again an enol ester, 2-(1-phenyl-3,3,3-trifluoro)-$\Delta^1$-propenyl benzoate (VII) was formed. The enol ester structure was proven by (1) hydrolysis of a sample with alcoholic aqueous sodium hydroxide to give a mixture of trifluoromethyl benzyl ketone, benzoic acid and phenylacetic acid[17]

---

[17] Had the acylation product been the isomeric C-acetylated derivative, *i.e.*, α-phenylbenzoyltrifluoroacetone, alkaline hydrolysis would have given a high yield of desoxybenzoin, but none of this ketone was obtained.

and (2) saponification with sodium methoxide to give a mixture of methyl benzoate and trifluoromethyl benzyl ketone.

## Experimental[18]

**Determination of the Products in the Reaction between Propiophenone and Methyl Trifluoroacetate.**—In all the acylations the earlier[3] apparatus was used. To a stirred suspension of 0.6 mole (34.2 g., 2.0 equiv.) of sodium methoxide in 200 ml. of absolute ether was slowly added (15 to 20 minutes) 0.3 mole (38.4 g.) of methyl trifluoroacetate in 50 ml. of anhydrous ether. Then, 0.3 mole (40.3 g.) of propiophenone in 50 ml. of anhydrous ether was added over a 40-minute period and the mixture was stirred at room temperature for a 20-hour reaction time, which is defined as the time interval between the start of the addition of the ketone and the hydrolysis of the reaction mixture. The mixture was then poured onto 500 g. of crushed ice and kept cold during the entire working up period by further additions of ice as necessary. The basic aqueous phase was extracted with three 200-ml. portions of ether and each extract washed with three 50-ml. portions of ice-water. The combined ether phases (extract I) were dried over Drierite. The ice-cold combined aqueous phases were cautiously acidified with a mixture of ice and concentrated hydrochloric acid, whereupon the β-diketone, α-methylbenzoyltrifluoroacetone, MBTA, precipitated as an oily solid. This acidified solution was extracted with three 200-ml. portions of ether and the combined extracts (extract II) dried over Drierite. The ether was distilled from extract I and the residue fractionated to give 11.5 g. of a mixture of propiophenone and methyl benzoate, b.p. 93–103° (20 mm.). Analysis of this mixture by quantitative infrared techniques showed it to consist of 6.4 g. (15.6% yield) of the ester and 5.1 g. (12.7% yield) of the ketone. The ether was distilled (ether distillate I) from extract II and the residue fractionated to give 41.8 g. (60.5%) of MBTA, b.p. 127–129° (20 mm.); copper salt, m.p. 210–212°. One-tenth of ether distillate I was treated with 2,4-dinitrophenylhydrazine (as described later for the preparation of the 2,4-dinitrophenylhydrazones of fluorinated ketones) and gave 1.12 g. of the 2,4-dinitrophenylhydrazone of trifluoromethyl ethyl ketone, m.p. 91–92°. Assuming quantitative conversion to the derivative, the total amount of fluorinated ketone present was 4.62 g. (12.5%). All the data listed in Table I were obtained using the procedure outlined above.

**Preparation of Other α-Substituted β-Diketones Containing the Trifluoromethyl Group.**—The reactions were executed using equivalents of the appropriate ketone and ethyl trifluoroacetate. Other pertinent data and the β-diketones prepared are found in Table II.

**Cleavage of α-Methylbenzoyltrifluoroacetone, MBTA, by Aqueous Sodium Hydroxide Solution.**—MBTA (0.2 mole, 46.1 g.) was refluxed for two hours with 200 g. of 20% aqueous sodium hydroxide solution, cooled to room temperature and extracted with two 50-ml. portions of ether. The combined ether extracts were dried, the ether distilled and the residue fractionated to give 25.0 g. (93.4%) of propiophenone, b.p. 104—105° at 20 mm.; 2,4-dinitrophenylhydrazone, m.p. 190–191°.[19] This distillate gave a negative test with alcoholic iron(III) chloride solution showing the absence of MBTA. The basic aqueous phase was acidified with concentrated hydrochloric acid and extracted with three 50-ml. portions of ether. The combined ether extracts were dried and the ether distilled. Only a small liquid residue (*ca.* 0.1 g.), which had an acrid odor and was probably trifluoroacetic acid, remained in the distilling flask.

**General Procedure for the Isolation of Perfluoroalkyl Alkyl Ketones.**—The procedures used for mixing the base and 0.3 mole each of the ester and ketone (Table III) and the apparatus used are the same as those employed in the acylation of propiophenone except that the mercury seal was replaced by a rubber slip seal. After the 20-hour reaction period, the reflux condenser was replaced by a condenser which was set for downward distillation and the ether was removed. The residue was heated at 40–50° in vacuum (20–40 mm.) for one hour. To the residue 100 ml. of toluene (in the synthesis of $CF_3COC_2H_5$ and $CF_3COC_3H_7$-*n*) or "xylol" (b.p. 135–144°) in the synthesis of $CF_3COC_5H_{11}$-*n* and *n*-$C_3F_7COC_3H_7$-*n*), 50 ml. of glacial acetic acid and just enough water to dissolve the sodium acetate formed were added successively. The phases were separated, the aqueous phase was extracted with three 50-ml. portions of toluene or "xylol" and the combined organic phases washed with cold saturated sodium bicarbonate solution to remove any perfluoroalkyl acid. The organic phase was distilled until the boiling point of toluene or "xylol" was reached. The distillate was then added dropwise through the top of a reflux condenser to 25 g. of phosphorus pentoxide contained in a flask, cooled by a mixture of ice and water. Subsequently, the liquid was decanted and distilled from fresh phosphorus pentoxide through a one foot concentric tube distillation column which was rated at sixty theoretical plates and the ketone collected. Thus, from a mixture of 0.6 mole (34.2 g.) of sodium methoxide, 0.3 mole (38.4 g.) of methyl trifluoroacetate and 0.3 mole (44.5 g.) of butyrophenone there was obtained 18.1 g. (43.0%) of trifluoromethyl *n*-propyl ketone, b.p. 65–67° (735 mm.); 2,4-dinitrophenylhydrazone m.p. 73–73.5°.

**Preparation of the 2,4-Dinitrophenylhydrazones of the Fluorinated Ketones.**—A mixture of 1.5 g. of 2,4-dinitrophenylhydrazine, 2 ml. of the fluorinated ketone and 100 ml. of 95% ethanol was heated to reflux temperature and then 2 ml. of concentrated hydrochloric acid was added and the mixture refluxed 15 minutes longer. About 50 ml. of alcohol was distilled and 50 g. of crushed ice was then added to the reaction mixture. If the 2,4-dinitrophenylhydrazone precipitated at this point, it was filtered and recrystallized from petroleum ether (b.p. 60–70°). If the derivative did not precipitate, the reaction mixture was extracted with petroleum ether (60–70°), the solvent distilled and the residue recrystallized, as bright yellow needles, from petroleum ether (60–70°). To recrystallize the low melting derivatives it was necessary to cool the petroleum ether solution of the 2,4-dinitrophenylhydrazone in a Dry Ice-acetone-bath.

**The Acylation of Trifluoromethyl *n*-Propyl Ketone with Benzoyl Chloride. The Synthesis of 2-(1,1,1-Trifluoro)-Δ²-pentenyl Benzoate (VI).**—To a stirred suspension of 0.1 mole (5.7 g.) of sodium methoxide in 200 ml. of absolute ether was added 0.1 mole (14.0 g.) of trifluoromethyl *n*-propyl ketone, dissolved in 50 ml. of anhydrous ether, over a 15-minute period. The mixture was stirred for 10 minutes longer, then 0.2 mole (28.2 g.) of benzoyl chloride in 50 ml. of anhydrous ether was added over a period of 30 minutes and stirring was continued for 17 hours at room temperature. The mixture was then poured onto ice and acidified with concentrated hydrochloric acid. The aqueous phase was extracted with two 100-ml. portions of ether, the combined ether phases dried, the solvent distilled and the residue fractionated to give 13.2 g. (54.1%) of VI, b.p. 121–123° (19 mm.). *Anal.* Calcd. for $C_{12}H_{11}O_2F_3$: C, 59.01; H, 4.54. Found: C, 59.19; H, 4.81. Compound VI gave neither a color test with alcoholic iron(III) chloride solution nor did its infrared spectrum show hydroxyl absorption, while its isomer, V, gave a positive enol test and showed hydroxyl absorption at 2.95 μ.

**The Cleavage of VI with Aqueous Alcoholic Sodium Hydroxide.**—In a 300-ml. flask equipped with a reflux condenser and a bubble counter were placed 0.041 mole (10.0 g.) of VI, 50 ml. of 95% ethanol and 0.2 mole (8.0 g.) of sodium hydroxide dissolved in 50 ml. of water and the mixture refluxed for two hours, during which time a gas, probably fluoroform, was evolved. Water (200 ml.) was then added, the basic reaction mixture extracted with three 50-ml. portions of toluene, the toluene extracts dried and the solvent distilled, leaving no residue. This shows that VI was completely cleaved. The basic aqueous phase was then acidified with concentrated hydrochloric acid and extracted with three 100-ml. portions of toluene. The combined extracts were washed with several portions of saturated sodium bicarbonate solution until acidification of the washings with hydrochloric acid no longer gave a precipitate. The toluene extracts were then processed as described above for the isolation of fluorinated ketones but no trifluoromethyl *n*-propyl ketone was obtained. The acidified bicarbonate washings were filtered to give a residue of benzoic acid (this was fused in vacuum at 20 mm.) and weighed 4.1 g. (81.8%), m.p. 120–121°, mixed m.p. with an authentic sample, 119–121°;

---

[18] All analyses were performed by Mr. George Stragand of the Microanalytical Laboratory of the University of Pittsburgh.

[19] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd Edition.

and a filtrate, which was saturated with sodium chloride, extracted several times with ether, the ether distilled and the residue fractionated to give 0.6 g. (16.6%) of *n*-butyric acid (formed by cleavage of $CF_3COC_3H_7$-*n*), b.p. 160–165°; anilide, m.p. 95–96°.[19]

**Cleavage of α-Ethylbenzoyltrifluoroacetone (V) by Aqueous Alcoholic Sodium Hydroxide.**—The previous reaction was repeated except that VI was replaced by an equivalent amount of its isomer, V. After the two-hour reflux period, during which no gas was evolved, 200 ml. of water was added, the basic aqueous phase extracted with three 50-ml. portions of ether and the extracts dried. After distilling the solvent, the residue was fractionated to give 5.3 g. (87.2%) of butyrophenone, b.p. 116–119° (20 mm.); 2,4-dinitrophenylhydrazone, m.p. 197–199°.[19] The basic aqueous phase was acidified with concentrated hydrochloric acid, extracted with ether and the extracts dried. After the solvent was removed only a small amount (0.2 g.) of a sharp smelling liquid (probably trifluoroacetic acid) remained. Thus, no benzoic acid was formed in this reaction.

**The Acylation of Trifluoromethyl Benzyl Ketone with Benzoyl Chloride. The Synthesis of 2-(1-Phenyl-3,3,3-trifluoro)-$\Delta^1$-propenyl Benzoate (VII).**—To a suspension of 0.3 mole (17.1 g.) of sodium methoxide in 200 ml. of anhydrous ether was added 0.3 mole (56.4 g.) of trifluoromethyl benzyl ketone over a 30-minute period. The ether refluxed rapidly during the addition of the ketone. After stirring for one hour, the reflux condenser was replaced by a condenser for downward distillation, the ether was distilled and the residue heated in vacuum (20–40 mm.) for one hour to remove the methanol formed in the reaction. Anhydrous ether (250 ml.) was then poured into the reactor and then 0.3 mole (42.2 g.) of benzoyl chloride, dissolved in 50 ml. of anhydrous ether was added dropwise over a 30-minute period and the mixture stirred at room temperature for one hour. The contents of the flask was then poured onto crushed ice and worked up as described above for VI to give 73.3 g. (83.5%) of VII, b.p. 123–127° (1.3 mm.), m.p. 47–48° (from 95% ethanol). *Anal.* Calcd. for $C_{16}H_{11}O_2F_3$: C, 65.75; H, 3.79. Found: C, 65.92; H, 3.83. Compound VII gave a negative enol test and did not form a copper salt.

**Cleavage of VII with Aqueous Alcoholic Sodium Hydroxide.**—In the apparatus used to cleave VI were placed 0.0342 mole (10.0 g.) of VII, 50 ml. of 95% ethanol, 0.2 mole (8.0 g.) of sodium hydroxide dissolved in 50 ml. of water and the mixture was refluxed for two hours, during which time a gas, probably fluoroform, was evolved. Water (200 ml.) was then added and the basic reaction mixture was extracted with two 50-ml. portions of ether. When this extract was dried and distilled, no residue remained. The basic aqueous phase was acidified with a mixture of ice and hydrochloric acid and extracted with three 100-ml. portions of ether. The combined ether extracts were washed with several portions of saturated sodium bicarbonate solution until the acidification of the washings no longer gave a precipitate. The ether extract was then dried, the ether removed and the residue distilled to give 0.7 g. (10.9%) of trifluoromethyl benzyl ketone, b.p. 164–167°; ammonia addition compound (recrystallized from benzene), m.p. 73–74°.[20] The acidified bicarbonate washings were filtered and the dried precipitate weighed 2.3 g. (m.p. 114–120°). One recrystallization from petroleum ether (b.p. 60–70°) gave 2.1 g. (50.3%) of benzoic acid, m.p. 121–122° alone and when mixed with an authentic sample. The filtrate from the filtered acidified aqueous phase was then extracted with three 100-ml. portions of diethyl ether and the combined extracts were dried and the solvent distilled. The crystalline residue weighed 4.0 g. (m.p. 49–112°) and was recrystallized from petroleum ether (60–70°) to give 1.8 g. (38.6%) of phenylacetic acid (formed by cleavage of $CF_3COCH_2C_6H_5$), m.p. 75.5–77° alone and when mixed with an authentic sample. The mother liquor from this last recrystallization was evaporated and gave 1.9 g. of solid material, m.p. 35–105°, which was probably a mixture of benzoic and phenylacetic acids.

**Cleavage of VII by Ethereal Methanolic Sodium Methoxide.**—To a suspension of 0.05 mole (12.9 g.) of sodium methoxide in 100 ml. of anhydrous ether were added successively 0.05 mole (1.6 g.) of absolute methanol and 0.05 mole (14.6 g.) of VII, dissolved in 100 ml. of anhydrous ether. After stirring at room temperature for two hours, the mixture was processed in the customary manner to give 5.4 g. (79.3%) of methyl benzoate, b.p. 90–91° (20 mm.), and 6.3 g. (67.0%) of trifluoromethyl benzyl ketone, b.p. 164–166°; ammonia addition compound, m.p. 75–76°.[20]

**Acknowledgment.**—The authors gratefully acknowledge the support of the United States Atomic Energy Commission during the course of this investigation.

---

(20) W. R. Nes and A. Burger, THIS JOURNAL, **72**, 5409 (1950).

PITTSBURGH, PENNSYLVANIA

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

# Organoplatinum Compounds[1]

BY HENRY GILMAN, MYRL LICHTENWALTER AND ROBERT A. BENKESER

RECEIVED NOVEMBER 22, 1952

The reaction of methylmagnesium iodide with anhydrous platinic chloride is complex, leading in part to the formation of tetramethylplatinum, trimethylplatinum iodide, dimethylplatinum diiodide and methylplatinum pentaiodide. Tetramethylplatinum can also be produced by the reaction of trimethylplatinum iodide and methylsodium. It does not react with benzoyl chloride or iodine, but is cleaved by hydrogen chloride forming trimethylplatinum chloride. Hexamethyldiplatinum, formed by the action of metallic potassium on trimethylplatinum iodide, reacts readily with iodine to form trimethylplatinum iodide.

The first organoplatinum compound, trimethylplatinum iodide, was synthesized by treating anhydrous platinic chloride with a large excess of methylmagnesium iodide[2]

$$PtCl_4 + 3\,CH_3MgI \longrightarrow (CH_3)_3PtI + 2MgCl_2 + MgI_2$$

Upon a careful study of this reaction it has been found far more complex than is indicated by the above equation. In addition to the trimethylplatinum iodide (I), there is formed tetramethylplatinum[3] (II), dimethylplatinum diiodide (VII) and methylplatinum pentaiodide (V). Two other platinum compounds were isolated which were not identified. It is noteworthy that with the possible exception of these unidentified products none of the haloplatinum compounds isolated contained chlorine. The following Flow Sheet illustrates the methods which were employed to isolate the products of this reaction.

---

(1) Paper LXXII in the series: "Relative Reactivities of Organometallic Compounds." The preceding paper is H. Gilman, R. G. Jones and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).

(2) (a) W. J. Pope and S. J. Peachey, *Proc. Chem. Soc.*, **23**, 86 (1907); (b) *J. Chem. Soc.*, **95**, 571 (1909).

(3) See R. E. Rundle, THIS JOURNAL, **69**, 1327 (1947), and R. E. Rundle and J. H. Sturdivant, *ibid.*, **69**, 1561 (1947), for a determination of the crystal structure of this compound.